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The low Frequency Components of the Spectrum of Wind-generated Waves[1]

O. M. Phillips and E. J. Katz

Mechanics Department
The Johns Hopkins University
Baltimore, Maryland

ABSTRACT

This paper is concerned with the dynamical processes involved in the growth of the ower frequency spectral components of wind-generated waves. Some calculations of Miles 1960) are extended, leading to the concept of a transition frequency for a given fetch as the requency above which energy is supplied to the waves by the instability (or sheltering) nechanism and below which it is supplied by the resonance mechanism. It is shown that if he fetch and duration of the wind is not large, the transition frequency is associated with a apid rise in the spectral magnitude, suggesting its identification with the frequency of the teep forward face of the spectrum. Reasonable confirmation of this is provided by a number f sets of published observations. It is also predicted that components whose frequencies are ear the spectral maximum are oriented more strongly in the wind direction than those at ower or higher frequencies. When the fetch and duration of the wind are large, the transi- ion frequency may be higher than the frequency of the spectral maximum. The compo- ients whose frequencies are less than the transition frequency acquire their energy by reso- ance with the convected surface pressure fluctuations. The resulting inferences concerning he directional distribution are discussed in relation to the two-dimensional spectrum meas- ired during the Stereo-Wave Observation Project (1957).

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1. *Introduction.* The shape of the spectrum of wind-generated gravity waves is determined by the interplay of a number of different physical mechanisms: the resonance between water surface and convected surface pressure fluctuations associated with atmospheric turbulence; the wave growth resulting from the 'sheltering'[2] effect of the waves; the nonlinear interactions among the wave components and the onset of dynamical instability of the water surface, leading to the formation of white-caps. In an earlier paper (Phillips, 1958a) it was shown that if the wind continues to blow, the high frequency components attain a state of saturation or statistical equilibrium, in which the net rate of energy supply to an interval of the spectrum just balances the rate of energy loss from the waves by the breaking process. In this equilibrium range, a dimensional analysis shows that the frequency spectrum is given by

$$\Phi(\omega) = \beta g^2 \omega^{-5}, \tag{1.1}$$

where ω is the radian frequency, g the gravitational acceleration, and β a dimensionless, absolute constant. There is now a good deal of observational evidence to support the relation (1.1). The earliest reliable measurements were made by Burling (1955) in Staines Reservoir, Middlesex, and his results led to a value of β of 7.4×10^{-3}. The results of Project S.W.O.P. (1957) showed that the high frequency components of ocean spectra, taken at a very large fetch and duration, follow exactly the same relation (Phillips, 1958b). More recent observations by Kinsman (1960) and Hicks (1960) are also in reasonably good accord with the form (1.1) at high frequencies.

In this paper we turn our attention to the components of the spectrum whose frequencies lie below the equilibrium range. This part of the spectrum frequently contributes most to the mean square surface displacement, very little being contributed to the mean square surface slope; thus a realistic first approximation to the dynamical behaviour of this range of the spectrum should be provided by the linearised theories of wave generation (Phillips, 1957; Miles, 1957). According to the resonance theory, energy is supplied to the waves by the convection of turbulent atmospheric pressure fluctuations across the water surface, the most rapid growth taking place when the convection velocities and length scales of the pressure pattern correspond to velocities and wavelengths of free gravity waves. Under this mechanism, the energy in any component of the wave system grows linearly with time. On the other hand, according to the instability theory, the wind blowing over the corrugated water surface sets up a surface pressure distribution that is in phase with the surface slope and is proportional to it, so that the energy in each component grows in the exponential manner characteristic of linearised instability models.

[2] The term is used here to describe the pressure variations induced by the air motion over a wavy surface (which have been estimated by Miles, 1957), without necessarily implying the presence of any region of flow separation in the lee of the waves.

t is shown in the following sections that the wave system is initiated by the esonance mechanism and that the energy in each component grows linearly ntil the component reaches a size whereon the instability mechanism can act fficiently, after which the energy grows approximately exponentially until onlinear effects become important. This appears to be the sequence of events or wave components whose phase velocity is much less than the wind speed t the height of about a wavelength. However, for the components whose peed is about the same as that of the wind, the instability mechanism is very nefficient (Miles, 1960); in other words, the 'sheltering' effect disappears. The bulk of the energy observed in these components must therefore be pro-ided by the resonance mechanism.

The interplay between these two mechanisms provides the theme of this aper, and the aim is to consummate the marriage of the two separate theories roposed by Miles (1960). This union enables us to explain quantitatively a umber of observed properties of wave spectra and to make further predictions hat lend themselves to experimental investigation.

2. *The Transition Frequencies.* In a recent paper, Miles (1960) has extended he analysis of wave generation by a surface distribution of fluctuating pressures et up by a turbulent wind (Phillips, 1957) to include to a first approximation he back reaction of the surface configuration upon the pressure distribution. Miles assumes that this induced pressure distribution is simply additive to he pressure fluctuations from the atmospheric turbulence and is given by

$$p_s(\mathbf{x}, t) = -\zeta \varrho_w c(k) \frac{\partial \xi(\mathbf{x}, t)}{\partial t}, \tag{2.1}$$

where ϱ_w is the water density, $c(k) = (g/k)^{1/2}$ is the phase velocity of free urface waves of wave-number k, ξ is the surface displacement, and the nu-erical parameter ζ represents the fractional increase in wave energy per cycle esulting from this pressure distribution. This last quantity, ζ, is given by Miles' tability analysis. When the velocity profile is logarithmic,

$$U(y) = U_1 \log\left(\frac{y}{z_0}\right), \tag{2.2}$$

where $U_1 = 2.5\, u_*$ (*i. e.*, 2.5 times the friction velocity) and where z_0 is the ffective roughness parameter, then the function ζ has the form

$$\zeta = \frac{\varrho_a}{\varrho_w} \left\{ \frac{U_1 \cos\alpha}{c(k)} \right\}^2 G\left(\Omega, \frac{U_1 \cos\alpha}{c(k)}\right). \tag{2.3}$$

n this last expression, ϱ_a represents the air density, α is the angle between the irection of waves propagation and that of the wind, and G is a numerically

determined function of $U_1 \cos\alpha/c(k)$ and of the additional parameter

$$\Omega = \frac{g z_0}{U_1^2 \cos^2\alpha}. \tag{2.4}$$

The functional dependence of G upon Ω is slight, so Miles suggests that littl error is introduced if the value 10^{-2} is chosen, this being the order of magnitud expected for this parameter when the short steep waves have attained thei equilibrium value.

Suppose that an infinite sheet of deep water is initially at rest and that a time $t = 0$ a turbulent wind begins to blow. If $\Pi(\boldsymbol{k}, \tau)$ is the spectrum of th turbulent atmospheric surface pressure fluctuations with time delay τ,

$$\Pi(\boldsymbol{k}, \tau) = (2\pi)^{-2} \int \overline{p(\boldsymbol{x}, t)\, p(\boldsymbol{x}+\boldsymbol{r}, t+\tau)}\, e^{-i\boldsymbol{k}\cdot\boldsymbol{r}}\, d\boldsymbol{r}, \tag{2.5}$$

the wave-number spectrum $\Phi(\boldsymbol{k}, t)$ of the surface displacement, generated b the combined influence of the turbulent fluctuations and the induced pressur variations (2.1), is shown by Miles (1960) to be of the form

$$\Phi(\boldsymbol{k}, t) = \frac{f(t, m)}{2\varrho_w^2 c^2(k)} \int_0^\infty \Pi(\boldsymbol{k}, \tau) \cos\omega\tau\, d\tau\,; \tag{2.6}$$

here

$$\left.\begin{aligned} \omega &= (gk)^{1/2}, \\ m &= \tfrac{1}{2}\zeta k c(k), \\ f(t, m) &= \frac{e^{2mt} - 1}{2m} \\ &= t\left\{1 + mt + O\left[(mt)^2\right]\right\}. \end{aligned}\right\} \tag{2.7}$$

The expressions (2.6) and (2.7) are of considerable interest. If $mt \ll 1$ $f(t, m) \approx t$, and (2.6) reduces to the expression given earlier (Phillips, 1957 for the generation of waves through the resonance mechanism by the atmos pheric turbulent pressure fluctuations alone. The components of the spectrun grow linearly with time. For a given wave-number $\boldsymbol{k}$ (in other words, for given m), as the wind duration increases the rate of growth increases from thi linear behaviour to an exponential one characteristic of an instability, th transition occurring at a wind duration t such that mt is of order unity. There fore we can define a transition wind duration for each wave-number such tha

$$T_t(\boldsymbol{k}) = m^{-1} = \left\{\tfrac{1}{2}\zeta k c(k)\right\}^{-1}, \tag{2.8}$$

about which the mechanism of wave generation changes from resonance t instability and the time history from linear to exponential. An interesting an

portant property is that T_t is independent of the magnitude of the atmos-
eric turbulent pressure fluctuations on the water surface.
Unfortunately, it is very difficult to make reliable observations under the
ration-limited conditions envisaged by this theory. A number of measure-
nts have been made, however, in fetch-limited situations, where an approxi-
tely steady wind blows from a clearly defined shore line for a time sufficient
ensure that the wave field is statistically steady in time. This fetch-limited
iation is complementary to the duration-limited case discussed in the theory,
d there exists a simple transformation between the two. For a given Fourier
mponent one might expect (a proof is given by Phillips, 1958d) that a
ration T is dynamically equivalent to a fetch F given by

$$F = \tfrac{1}{2}\, c\,(k)\, T \tag{2.9}$$

linearised waves; here $\frac{1}{2}\, c\,(k)$ is the speed of energy propagation, or the
oup velocity. The expression (2.9) is valid when $F \gg \lambda$, the wavelength of
e component in question, and this condition is always amply satisfied in our
nsiderations. Observations at a fixed fetch are conceptually equivalent to
servations over an ensemble of duration-limited wave fields originating at
ne previous instant. For a fixed fetch, the equivalent duration is different
different wave-numbers, k, or frequencies, n, since the group velocity is
function of k or n.
It is convenient, then, to translate the expression (2.8) into one giving the
ch F_t at which transition occurs for a given wave-number. From (2.9),
e have

$$F_t(\boldsymbol{k}) = \frac{\frac{1}{2}\, c\,(k)}{m} = \{\zeta\, k\}^{-1},$$

that the number of wave-lengths travelled by a component of the wave
tem before transition is simply

$$\frac{F_t(\boldsymbol{k})}{\lambda_t} = (2\,\pi\,\zeta)^{-1}, \tag{2.10}$$

hich, from (2.3) is a function of $U_1 \cos\alpha/c\,(k)$. The continuous curves of
g. 1 were derived from Miles' (1960) calculations; Ω is taken as 10^{-2},
$\varrho_w = 1 \cdot 2 \times 10^{-3}$, and the 'wind speed' U is defined as $9\, U_1$ to correspond
the wind speed as usually measured several meters above the surface. It is
ar that for a given frequency and an increasing fetch, the transition occurs
liest when $\alpha = 0$, or for the wave components travelling in the direction
the wind.
These relations can be interpreted inversely. For a given fetch, there is a
nsition frequency below which energy is supplied to the waves by the

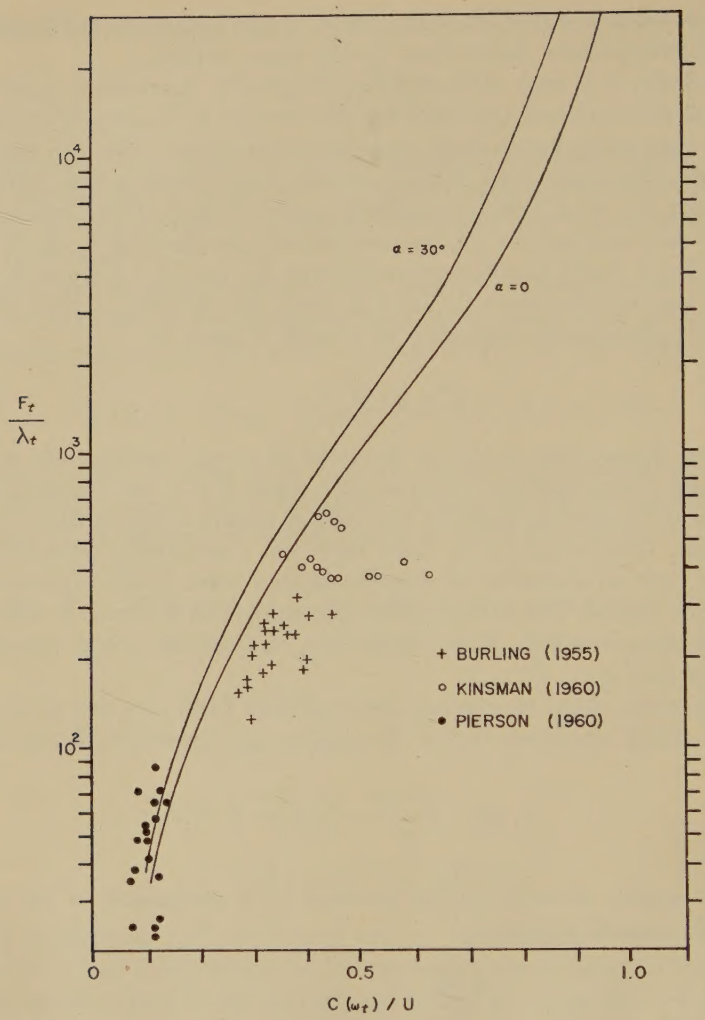


Figure 1. The number of wavelengths of wind-generated waves before transition.

atmospheric turbulent pressure fluctuations and above which (for componen travelling in the wind direction) energy is supplied by the 'sheltering' effe associated with the instability.

Let us now inquire whether this transition might be related to some o servable property of the spectrum of wind-generated waves. The natu of the transition is such that the wave growth begins to accelerate rapidl until nonlinear or surface stability effects become significant. Now, a ve characteristic property of frequency spectra measured at a point is that t

ctral density rises quite abruptly from low frequencies to a maximum and n falls off more gradually (approximately as ω^{-5}) as the frequency increases. the fetch increases, the frequency at which this forward face is found creases; or conversely, if we consider one particular frequency of the spec- m, for increasing fetch, *the value of the spectrum rises rapidly with increasing ch* as the steep forward face moves past our observation frequency to lower ues. This is exactly the property expected as a result of the transition from owth dominated by the resonance mechanism to one dominated by an tability; and it strongly suggests an identification between the frequencies the steep forward face of the spectrum at various fetches and the transition quencies that emerge from the theory.

It should perhaps be pointed out that the theory contains no adjustable rameters, so that any discrepancies between theory and experiment must be ributed to a lack of correspondence between the conditions of observation d those envisaged by the theory.

3. *Some Observations at Short and Moderate Fetches.* Let us therefore com- re the transition frequencies inferred above with the frequencies of the steep ward face measured in recent observations. Three sets of measurements, ade at short or moderate fetches, appear to be reasonably suited to our pur- se; the minimum requirements are moderately well defined conditions of servation and the measurement of detailed spectra. These are the results Burling (1955), Kinsman (1960) and W. J. Pierson[3]. A disadvantage of three is the lack of detailed wind measurements, though Kinsman (1960) es give a little information on the profiles.

The frequencies at which the spectral density rose abruptly were taken from e individual spectra, of which Fig. 2 is a representative sample. Since the rise as abrupt in almost all cases, there was little possibility of significant subjective ror. From these frequencies, the corresponding phase speeds and wavelengths ere calculated. Since transition occurs first for the components travelling in e direction of the wind ($\alpha = 0$), the fetch was in each case taken as the dis- nce to the upwind shore.

The data taken from these three sources are shown in Fig. 1, where the served frequencies of the steep forward face are certainly of the same order magnitude as the predicted transition frequencies. The scatter however is nsiderable and the range of values of F_t/λ_t over which observations were ade is limited. There are probably a number of reasons for the large scatter the observational points, despite the considerable precautions taken in each se to ensure that the wind was approximately steady in magnitude and direc- n. In the first place, Miles' (1957, 1960) calculations for the function sume that the wind velocity profile is logarithmic, whereas Kinsman's (1960)

3 Mr. Pierson's measurements have not yet been published. We are grateful to him for his permis- n to use these data.

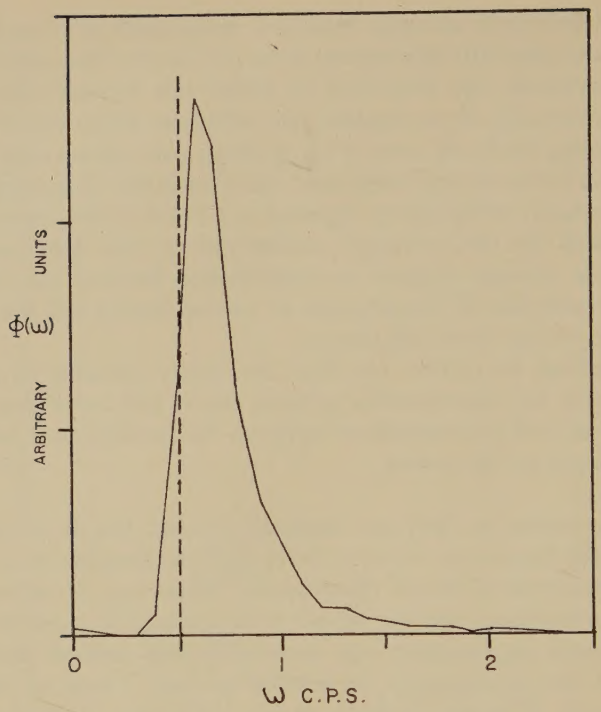


Figure 2. A typical spectrum of wind-generated waves at short fetches: Kinsman's (1960) record oc
The broken line indicates the frequency of the steep forward face.

wind data, taken simultaneously with the wave data, show that in many cas the actual profile differed considerably from the logarithmic form. The ana ysis of Benjamin (1959) shows that different (but not implausible) veloci profiles can result in a variation of order 50% of the theoretical curve f F_t/λ_t at a given c/U. Furthermore, the analysis envisages the motion as starti from rest. If, in the experiments, there is any background wave motion ne the windward shore, the transition for a given frequency will occur at a short fetch. Since the wave growth under the influence of the turbulent pressu fluctuations is relatively slow under these conditions (small c/U), even a sm background would have a significant effect and would result in the observ tional points lying below the theoretical curve, as indeed do most of Burlin and Kinsman's results.

Pierson's measurements were made in a water tank mounted in a lar wind tunnel. Detailed velocity profiles near the water surface were not mea ured. At these short fetches and low values of c/U, the function ζ depen critically upon the form of the profile very near the water surface[4]. Sm

4 If $u(y)$ is the wind profile, ζ is approximately proportional to $u''(\Upsilon)$ where Υ is the height wh $u(\Upsilon) = c$ (Miles, 1957).

itions in the profile will therefore result in very different transition fre-
ncies, since the observations depend very sensitively on a flow property
is very difficult to control. The considerable scatter in Mr. Pierson's
rvations can probably be attributed to this cause, but it is noteworthy that
oints do straddle the calculated curve of Fig. 1.
seems, then, that in view of the uncertainties inherent in the observations,
agreement is as good as can be expected; and the interpretation of the
uency of the steep forward face of the spectrum under these conditions
ne transition frequency is likely to be correct. Since almost all of the wave
gy is at frequencies higher than the transition frequency, it follows that
t of the energy has been supplied to the waves under these circumstances,
he 'sheltering' or instability mechanism or by the pressure variations in-
d by the flow of air over the waves. These circumstances are by no means
ersal, as we show in the next section, but, on the basis of the theory and
observations so far available, we might expect similar behaviour for small
noderate fetches (the experiments described above range to about 1500 m)
all except very light winds. Our conclusions here seem to provide the
ect explanation for Cox's (1958a) failure to observe the directional peaks
ciated with the resonance theory in a tank experiment. Sirce c/U was
ll in his experiment, the resonance mechanism only provided a trigger
the growth of the instability, so that the resonance maxima at angles
$^{-1}\, c/U$ to the wind direction would be entirely obscured. Earlier remarks
this subject (Phillips, 1958c: 228) are probably of lesser significance.

The conclusions reached here make possible a further prediction. The
sition to an exponential rate of growth occurs first when $\alpha = 0$, irre-
tive of the form of the turbulent pressure spectrum. If this results in a
d growth of these spectral components and a steep forward face of the
e spectrum, then it follows that the components having frequencies near
spectral maximum should have propagation directions oriented strongly
ards $\alpha = 0$. For frequencies greater than the ones near the spectral peak,
sition will have occurred for components whose propagation directions
er a wider angle. These components also grow rapidly and may attain
r saturation value; in any event, the directional distribution of the com-
ents at these frequencies will, according to these ideas, be much broader.
s prediction appears to be in qualitative accord with casual observations of
d-generated waves at short or moderate fetches. A detailed experimental
y along these lines has not yet been undertaken, though it seems feasible,
it would be decisive in establishing the significance of this transition.

. *Observations at Large Fetch and Duration.* It is fairly evident that the
ussion of the previous section does not include all cases of interest. If the
h or duration of the wind is very small, the instability or sheltering me-
nism has no opportunity to operate at any frequency, and any waves gener-

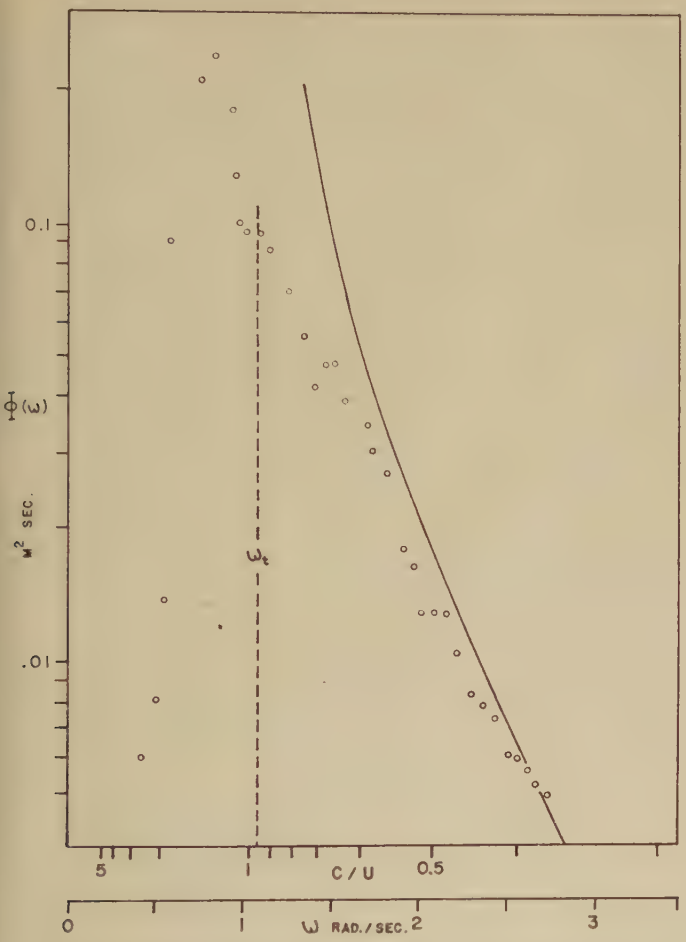
ated must be attributed to the resonance mechanism. The early observat of Roll (1951) at fetches of a few meters are consistent with this rem

It seems paradoxical at first that the resonance mechanism is capabl contributing significantly also when fetch and duration of wind are both large. The reason is, that for wave components whose phase velocity is proximately equal to the wind velocity, the 'sheltering' effect is very w Fig. 1 shows that the transition fetch is of order $10^4\lambda_t$ or greater. On other hand, the resonance mechanism operates most effectively under t same conditions, so that the spectral density for these components, increa linearly with fetch or duration, may approach the saturation value before transition fetch or duration is attained. Components travelling at the s speed as the wind, or faster, are unable to extract any energy from the w by the instability mechanism; indeed, they may even supply energy to wind by a 'negative sheltering', so that, if any such components are obser they must be attributed either to the resonance mechanism or to the eff of 'sheltering' by intermittent gusts of wind with velocity much greater t that of the mean wind.

A number of observational studies have suggested that when the fetch duration of the wind are both large, components for which c/U is of o unity may contribute significantly to the mean square wave height. The i situation would be one in which the wind field is approximately steady uniform over a wide expanse of open ocean, but few of the observations av able at present approach these requirements. The most suitable for our p pose seem to be the results of the Stereo-Wave Observation Project (19 The waves were generated primarily by a wind of some 20 knots which approximately steady for about 18 hours; the frequency spectrum, measu by a wave pole, is shown in Fig. 3. The transition frequency ω_t under t conditions is shown in this diagram and falls at a frequency greater than of the spectral peak.

The simplest interpretation of the dynamical processes involved is that, frequencies less than ω_t, including those near the spectral peak, the w energy has been acquired from the wind by resonance with the the atmosph turbulent pressure fluctuations; and for frequencies greater than ω_t, ene is currently being supplied by the 'sheltering' mechanism or by the wa induced surface pressure fluctuations. For frequencies greater than ω_t, spectrum is very near its equilibrium or saturation value, so that the ene being continually supplied by the latter mechanism can result in little fur wave growth. Some of it is doubtless transferred to other spectral compon by nonlinear interactions, but most will ultimately be lost to the waves thro the formation of white-caps.

The alternative to this is to postulate that the forward face of the S.W.C spectrum is still the result of the transition to an unstable rate of growth. equivalent fetch for this spectrum is of order 200 miles so that, if λ is



ure 3. The frequency spectrum for the S.W.O.P. wave-pole data. The solid curve represents the equilibrium range asymptote, the broken line the transition frequency w_t.

elength of the components near the forward face, $F/\lambda \sim 4 \times 10^4$. Fig. 1 s that the transition frequency is therefore such that $c/U = 0.98$. This rn implies that the wind speed U used in the upper scale of Fig. 3 was small. In order that $c \simeq U$ for frequencies near the forward face, it is ssary that the wind speed be greater by some 70% over the entire gener- area than the authors of the S.W.O.P. report believed. The existence ch a large error as this strains the credulity of even the present authors, this alternative hypothesis seems untenable.

appears to be inevitable, then, that our first interpretation is the correct and that the wave energy present in the components of frequency less

than ω_t has been acquired by the resonant interactions between the w and the convected turbulent pressure fluctuations on the surface. Ther also other evidence that points to the same conclusion. If these compon are generated by the resonance mechanism, then the directional distribu of the components at a fixed scalar wave-number k, or a fixed freque would be expected to possess maxima at angles $\cos^{-1}\{c(k)/U\}$ to the w direction. For these components, the resonance condition is satisfied exa (Phillips, 1957) and the growth is most rapid. The two-dimensional spe as measured in the S.W.O.P. project do indeed show directional maxima o to the predicted angles (Phillips, 1958b), over frequencies of order ω_t and Although, as Cox (1958b) pointed out, the existence of these maxima is by itself completely conclusive, it now appears to be quite consistent w these new results. The presence of the directional maxima is predicted by theory in a natural manner and does not require postulation of the existe of two distinct wind systems of relatively high velocity.

The transition frequency ω_t shown in Fig. 3 has another interesting asp Near the transition frequency, the rate of energy transfer from the win the waves is greatly enhanced by the operation of the sheltering mechan although the magnitude of the spectrum cannot increase beyond the equ rium range value because of the requirements of surface stability. The in esting possibility suggests itself that the small rise in the S.W.O.P. spect at this frequency represents the remnant of the steep forward face foun smaller fetches and durations that has largely disappeared through the gro of lower frequency components by the resonance mechanism.

The roles played by the various dynamical processes, inferred by examina of the S.W.O.P. data in the light of the wave generation theories, are pected to be characteristic of those operating when the fetch and duratio the wave field is large and when components are present that travel at al the same speed as the mean wind. It is difficult to estimate at this stage how large the fetch and duration must be in order that the transition freque lie above the frequency of the spectral peak. This depends on the magni of the turbulent surface pressure fluctuations that generate wave compon whose phase speed is near the wind speed, and about these we have little formation. Among other effects, we might expect that the stability of lo layers of the atmosphere would be important, since unstable conditions re in higher turbulent intensities, hence larger surface pressure fluctuations.

We are very grateful to Dr. Blair Kinsman for the stimulating discus we have shared on these matters.

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The Physiological Ecology of a Marine Diatom, Skeletonema costatum *(Grev.) Cleve*[1]

Herbert Curl, Jr., and Guy C. McLeod[2]

Woods Hole Oceanographic Institution
Woods Hole, Massachusetts

ABSTRACT

The marine plankton diatom, *Skeletonema costatum*, was isolated from local waters a cultured in enriched sea water. The effects of light, temperature, salinity, and concentrati of phosphorus and nitrogen on its growth and photosynthesis were determined separat and simultaneously. The effects of exocrine production by *Skeletonema* and grazing copepods also were tested. The experimental results were used in developing an index the photosynthetic potential of the diatom for seasonal hydrographic conditions found in continental shelf waters south of Long Island.

Experimental results indicated that *Skeletonema* should have high photosynthetic ra and rapid cell division in late summer and early winter on the continental shelf by vir of its responses to light and temperature alone. The usual concentrations of phosphorus a nitrogen on the shelf should not be limiting to this diatom.

The distribution and abundance of *Skeletonema* in 1956–1957 appeared to be in acc with predictions of potential photosynthesis except in offshore waters. Calculated pho synthetic rates and large standing crops occurred in late summer, decreasing toward winter. The highest calculated photosynthetic rate in inshore waters was 29 % of the ma mum rate, in July. The lowest calculated rates were for March through May.

Although the diatom ought to grow well offshore, it does not, apparently due to insu cient light during winter to support a stock for later growth. There is evidence that the l of an undetermined nutrient also limits growth offshore.

Introduction. In natural phytoplankton populations, one algal species f quently predominates in numbers of individuals or in biomass. Such a situati may be taken as an indication of successful adaptation to prevailing enviro mental conditions, whether or not the species is an ecological dominant, the sense of Shelford and Towler (1925). It should be possible to predict physiological characteristics of an organism from its responses to the enviro

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[2] Present address: Carnegie Institute of Washington, Palo Alto California.

nt or, conversely, predict its responses in nature from physiological behavior laboratory studies.

Frequently species that are important constituents of natural phytoplankton ulations are singularly difficult to culture. However, *S. costatum* frequently major component of plankton blooms and grows extremely well in culture. s present as far north as Thule, Greenland, and along the coast of the Gulf Maine it is abundant and often "dominant" in summer and autumn (Bigelow 26). It is the primary species in lower Narragansett Bay (Smayda 1957), ng Island Sound (Conover 1956) and Block Island Sound (Riley 1952), has been very abundant in Chesapeake Bay (Cowles 1930) and at Beaufort, rth Carolina (Manly 1953). In the Gulf of Mexico, it is abundant in spring autumn though seldom if ever a primary species (Curl 1960). It seems to ur wherever plankton has been studied in coastal areas, except in the Arctic Antarctic seas.

S. costatum was isolated in unialgal culture from Woods Hole Harbor in ne 1957. Experiments were performed to study its responses to some of chemical and physical variables important in local waters. Simultaneously, anographic cruises on the continental shelf south of Long Island yielded ormation on its distribution and abundance in natural populations, and ociated hydrographic data. This paper correlates these laboratory and field ervations.

Methods and Materials. *Skeletonema* was grown in enriched sea water w), the composition of which is given in Table I. Sea water from Vineyard und, with an average salinity of 31 °/₀₀, was filtered through a Millipore A filter, enriched and autoclaved; its pH was 7.9–8.0 and its CO_2 con-ntration of 1.84 mmole; a five day supply of carbon at the maximum growth es and cell concentrations used. The cultures were kept at 19–21°C under ,000 lux illumination, and subcultures were made every fifth day. Rapidly owing cells, forming long chains, were used in the experiments.

TABLE I. Concentration of Enrichment Additives in ESW Medium (Formulated by J. H. Ryther).

Compound	Concentration	
	g/100 ml	mol. conc. μg-at/l
NO_3	0.01	1000 NO_3–N
$H_2PO_4 \cdot 12\ H_2O$	0.002	50 PO_4–P
$Na_2SiO_3 \cdot 9\ H_2O$	0.0005	–
$Na_2S_2O_3$	0.00012	–
ferric citrate	0.0003	–
citric acid	0.0003	–
vitamin B_{12}	0.12	–
soil extract	0.5	–

Photosynthesis was measured by uptake of C^{14} according to the metho of Steeman Nielsen (1952) as modified by Ryther (1954). The rates are ex pressed relative to the maximum value obtained in an entire series of exper ments. The photosynthetic rate was determined after the cells had been expos to the experimental conditions for periods which in different experimen lasted five or more days. The rates are therefore representative of the fin experimental conditions in the culture.

Results

Salinity. The effect of salinity on the rate of photosynthesis was studi in the range from 5–45‰. The Vineyard Sound sea water (31‰) w diluted with distilled water to give more dilute solutions; dried salt from loc sea water was added to give higher concentrations.

Photosynthesis experiments, made one week after inoculation, showed t highest photosynthetic rates per cell at 15‰ (Fig. 1). Considerable toleran to higher salinities was evident. Throughout the salinity range of 11–40‰ the rate of photosynthesis was at least half that of the maximum. When t salinity of the sea water was adjusted without adding nutrients, maximu photosynthesis occurred at 20‰. Both salinity and nutrients were diluted the unenriched experiments, which may explain the lack of photosynthe below 10‰. Carbon dioxide should not have been limiting at this concentr tion since 0.63 mmole/l was present initially.

Light and Temperature. Photosynthesis by cultures of *Skeletonema* logarithmic growth phase was measured at temperatures from 5–30°C at lig intensities varying from 0 to 36,000 lux. The incident light was attenuat

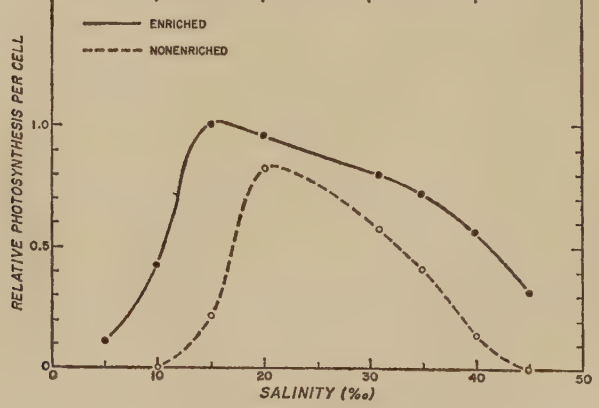


Figure 1. Relative photosynthesis in enriched and nonenriched sea water of varying salinities.

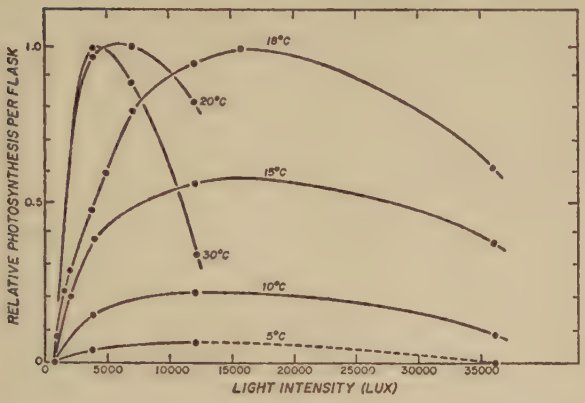


Figure 2. Relative photosynthesis as a function of light intensity at various temperatures.

h flat spectral distribution, neutral density filters. Replicates did not vary more than 10%; averages are plotted in Fig. 2. The point at which apparent o photosynthesis occurs is the compensation intensity. In these experiments of the curves can be extrapolated to a compensation intensity of about 50 lux.

At temperatures ranging 5–18°C, light saturation occurred at 12,000 to 000 lux. Below 18°C the rates decreased with temperature, but light saturon still occurred from 12,000 to 16,000 lux. Above 18°C the saturation ensity was reduced to 4,000–6,000 lux, and the range in which maximum tive photosynthesis took place became very narrow. The decrease in photothesis at high light and temperature may be a result of greatly enhanced respiration. Matsue (1954) found that the highest temperature tolerated *Skeletonema* was between 37° and 40°C.

Nutrients. Experiments were conducted to determine the effect of varying centrations of phosphorus and nitrogen upon photosynthetic ability. After ulture had passed the logarithmic phase of growth and the cells could be sumed to be deficient in nutrients, aliquots were inoculated into an ESW lium containing varying concentrations of phosphorus and nitrogen. After days growth at 18°C and 8,000 lux, C^{14} was added and carbon uptake measured at the end of two hours (Fig. 3). The rate of photosynthesis was ner with enrichment by either nitrogen or phosphorus concentration; for phosphorus concentrations the increase in rate of photosynthesis as a func- of nitrate increment was about equal. Since these experiments measured "population" photosynthesis rates, the rates could increase with higher rient concentrations almost indefinitely as more biomass was produced. e scale of relative photosynthesis for the entire nutrient concentration

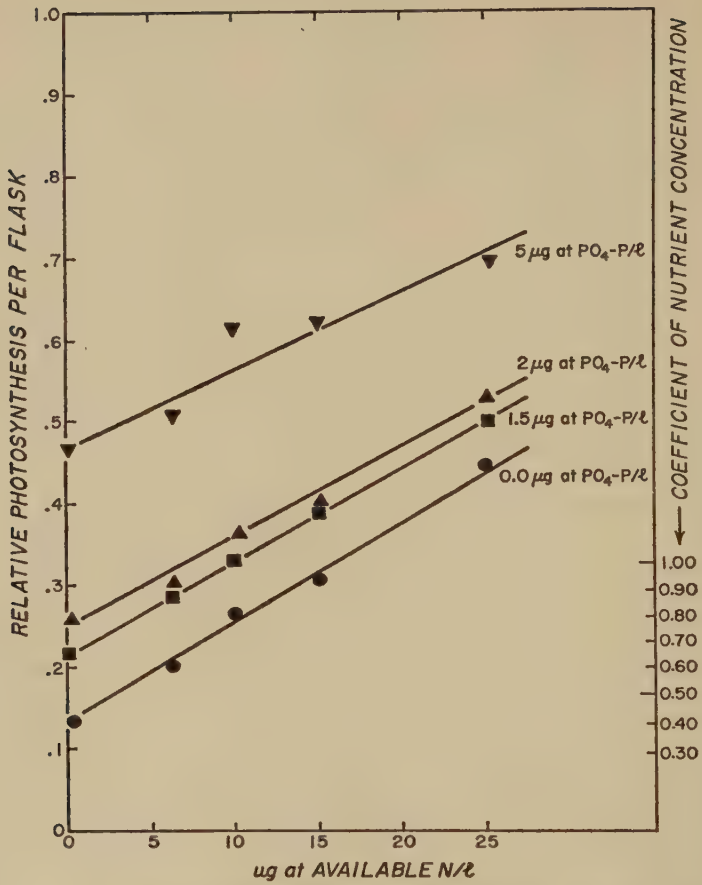
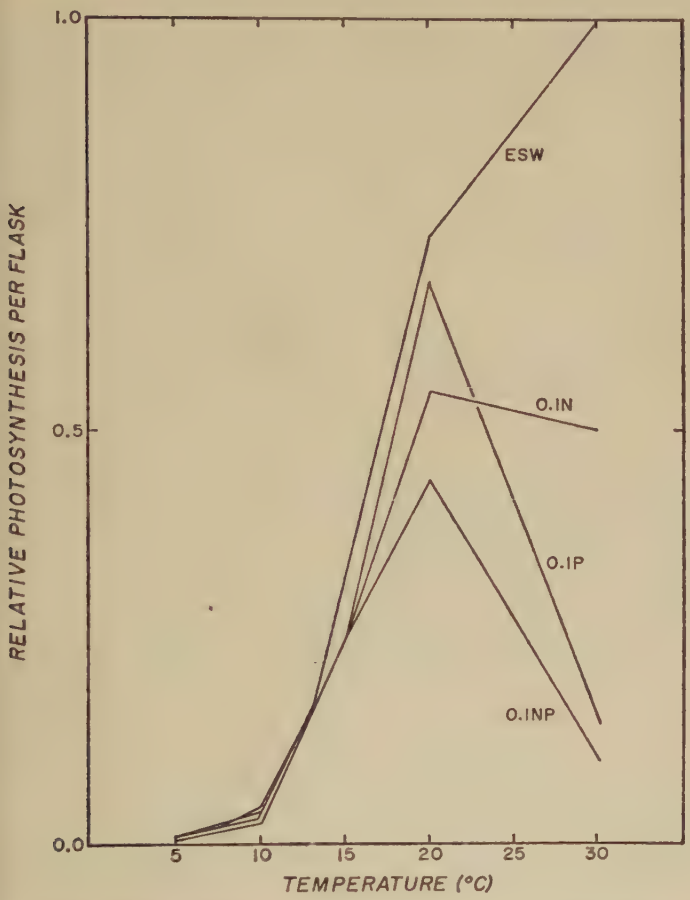


Figure 3. Relative photosynthesis as a function of low concentrations of phosphate phosphorus available nitrogen. A scale of nutrient concentration coefficients replaces the scale relative photosynthesis on the ordinate (see text).

range of the experiments has been discarded and a scale of nutrient concent tion coefficients has been used in its place. The lower limit has been set at z concentration. In order to have a coefficient of nutrient effect in the ra 0–1.0, the upper limit has been set at the largest concentrations of phospho and nitrate that normally might be encountered in coastal Atlantic wat (0–1.0 μg-at available N/l, 0–1.5 μg-at PO_4–P/l) (Ketchum, *et al.* 1958).

Nutrients and Temperature. The effects of reduced amounts of nutrie on photosynthesis were studied at temperatures ranging from 5–30°C a single light intensity (10,000 lux). Nitrate and phosphate were reduced to the usual concentration, both separately and together. After inoculation fr



ure 4. Relative photosynthesis as a function of temperature and nutrient concentration at 13,000 lux.

o-week old stock cultures, deficient in both phosphorus and nitrogen, the w cultures were equilibrated at the new temperature conditions for two ys and then carbon fixation was measured for a two-hour period. Photo-nthesis was at a maximum at 20°C at all nutrient dilutions (Fig. 4). The ect of reduced nitrogen alone was greater than reduced phosphorus at 20°C. ne effect of reduced nutrients was greatest at the higher temperatures.

Studies of cell division rates at temperatures from 5–30°C were made at ,000 lux in a complete medium and in a medium deficient in nutrients able II). Aliquots of a week-old culture growing in the ESW medium re inoculated into the ESW medium and into media deficient in nutrients, used in the previous experiment. Cell counts were made daily until moribund

TABLE II. Maximum and Average Division Rates During the Logarithmi Growth-Phase of *Skeletonema costatum* Grown at 10,000 Lux and A Various Temperatures and Nutrient Concentrations for One Week

Medium	ESW		10% P		10% N		10% NP	
Temp. °C	max.	av.	max.	av.	max.	av.	max.	av.
30	4.28	0.94	3.17	1.02	4.25	1.19	1.35	1.05
20	4.28	1.21	3.45	1.35	4.35	1.22	3.17	1.24
15	3.17	1.24	3.27	1.28	3.17	1.24	1.66	0.89
10	–	0.47	–	0.50	–	0.51	–	0.51
5	–	0.21	–	0.0	–	0.08	–	0.01

* Division rate $k = \frac{1}{(t_2-t_1)} \log_2 \frac{C_{t2}}{C_{t1}}$, where t = time in days and C_{t1} and C_{t2} are c counts at beginning and end of the time (t_2-t_1).

cells were noted. The maximum and average division rates for the logarithm portion of the curves are given in Table II. In the ESW medium the max mum division rate was 4.28 divisions per day at 20 and 30°C. This is the sam value determined by Matsue (1954).

In a medium containing reduced phosphate, the fastest maximum divisio rate was observed at 20° (3.45) and the slowest at 30°C (3.17). The divisio rates in reduced nitrate were equivalent to those in full strength mediun Thus, decreased phosphate concentration was more effective than decrease nitrate concentration in lowering the division rate.

In reduced nitrate and phosphate, the division rates were lower than i any of the cultures maintained between 15° and 30°C. Under nutrient d ficient conditions, the optimal temperature range for rapid cell division becom narrower (stenothermal with respect to rate of cell division). The followin division rates are recorded in the literature: 0.21–1.77 div./day during wint in nature (Riley 1952), 0.90–2.6 div./day at 10°C in culture (Braarud 193 1945).

Exocrines. In order to determine whether *Skeletonema* produces substanc affecting its own growth or that of other algae, several liters of a week-o culture were centrifuged and the supernatant millipore-filtered. The filtra was re-enriched and half was autoclaved for half an hour. Subcultures usin both autoclaved and nonautoclaved aliquots were inoculated with *S. costatu Chaetoceros ceratosporum*, *Corethron hystrix*, *Ditylum* sp. and *Phaeodactylu tricornutum*. Cell counts were made after inoculation and again after sev days incubation at 18°C under 7,000 lux (Table III).

In the autoclaved medium, *Skeletonema*, *Ditylum* and *Phaeodactylum* ma good growth, *Chaetoceros* perished and *Corethron* grew slowly. In the nonaut claved medium, *Chaetoceros* and *Ditylum* grew not at all and *Corethron* a *Skeletonema* required seven days to double their numbers. *Phaeodactylu*

TABLE III. Comparison of Seven-Day Growth Rates at 18°C, 7,000 Lux; Algae in Autoclaved and Nonautoclaved Filtrate from *Skeletonema* Cultures.

Diatom	Initial cell count (cells × 10^4/ml)	ESW	Division per day	
			autoclaved	nonautoclaved
eletonema costatum	4.0	1.2	1.1	0.04
aetoceros ceratosporum	0.75	1.0	0.0	0.00
rethron hystrix	0.25	–	0.57	0.12
tylum sp.	0.03	–	0.81	0.00
aeodactylum tricornutum	2.2	1.0	1.0	0.60

owed the best growth, but this was equivalent to only 0.6 div./day. *Skeletonema* elf was also severely inhibited. *Chaetoceros* ordinarily grew well in an ESW edium but appeared to be extremely sensitive to substance(s) produced by *keletonema*.

Grazing. When plankton tows containing large quantities of *Skeletonema*, gether with *Rhizosolenia*, *Nitzschia*, *Guinardia*, *Thalassionema*, and *Chaeto-ros*, were set aside in the culture room, copepods (mainly *Acartia tonsa* and *seudocalanus* sp.) rapidly reduced the numbers of *Skeletonema*, leaving uneaten lls of *Rhizosolenia* which rapidly outgrew the other genera. *Skeletonema* emed to be the favored food among the diatoms available, so far as these vo species of copepods were concerned.

DISCUSSION

In comparing laboratory and natural populations, the environmental re-onses of an organism may be considered from different points of reference. n one, optimal growth conditions are determined in the laboratory and then milar conditions are sought in nature. Large populations would tend to occur here such conditions were found, and smaller populations elsewhere. How-ver, the environmental and physiological conditions of the organism are anging with time. Riley, *et al.* (1949) attempted a prediction of productivity nature based on laboratory results, taking these changing conditions into count by substituting into a differential equation.

Here an attempt is made to evaluate the potential productivity of *Skeletonema* the continental shelf, on the basis of laboratory results, by determining the otosynthetic rates under the physical and chemical conditions obtaining at onthly intervals throughout the year. The potential or "predicted" pro-uctivity rates may be compared with the actual abundance and distribution the populations in nature.

In our experiments, light and temperature were factors that interacted in ch a way that they should be considered simultaneously. Salinity and the

concentrations of available nutrients affect the photosynthetic rate, and th initial concentrations of phosphate and nitrate determine the size of the standin crop. *Skeletonema* inhibits its own growth when grown in dense cultures Finally, the alga is consumed readily by some copepods.

To obtain data for natural conditions, the effects of salinity, light, temper ature and nutrients on the potential photosynthesis of *Skeletonema* have bee evaluated for the coastal waters south of Long Island, where observation were made during six cruises between September 1956 and September 1957 The data for adjoining stations have been combined and averaged over th depth of the wind-mixed layer, as determined by the pycnocline. This has bee done separately for three depth ranges, *i. e.*, stations in water less than 100 m deep, between 100 and 500 m, and over 500 m. Values for months durin which no observations were available were interpolated from smoothed sea sonal curves.

For each group of stations the combined effect of light and temperatur (Fig. 2) was determined as a per cent of the maximum photosynthesis obtaine in the experiments (relative photosynthesis). Subsequently, the separate effect of salinity (Fig. 1) and of phosphate and nitrate (Fig. 3) were evaluated; th cumulative effects given by the product of each successive factor provided th potential productivity.

The average light intensity in the mixed layer was derived from the formul of Riley (1957), using Kimbal's (1928) tables. These data were reduced b 50% to eliminate the energy from wavelengths not available for photosynthesis They have been converted from energy to intensity units by the relationship 1 g cal/cm^2/min = 155×10^3 lux (Ryther 1956 b). The duration of daylig was taken from Baker (1938). Light attenuation coefficients were obtaine either by secchi disc reading or by submarine photometer.

At the shallow stations (Table IV), on the basis of light and temperatur alone, the highest potential photosynthetic rates occurred in July and Sep tember (72%) and the lowest in midwinter (3–7%). Introduction of th salinity effect decreases all monthly values without fundamental change in th pattern. The combined effect gives a maximum value of 57%, and a minimu of 2.3%. The nutrient effect further reduces these to 26% and 1.5%. Th same analysis has been applied to the results from the "intermediate" and dee stations (Tables V and VI). The cumulative effect of all factors shows tha during most of the year the potential photosynthetic rates were higher at th intermediate stations than inshore. The potential ranged from 3–32% at th intermediate stations. At the deep stations the potential rates ranged from zer in winter, when the mixed layer was very deep, to values as high as 29–34% in summer and autumn.

The standing crops of *Skeletonema* observed in this case are shown in Fig. 5 The large populations observed from September through February correspon with the calculated high potential photosynthesis rates for the beginning o

TABLE IV. The Fractions (P) of Maximum Photosynthesis Computed Successively for Temperature and Light (t, i), Salinity (s) and Nutrients (n). The Cumulative Effect (Potential Photosynthesis) is Given by the Product of These (Ptisn).

Data for Stations with Water Depth of 100 m or Less.

Date†	Light (lux)	Temp (°C)	P_{ti} (%)	Salinity (‰)	P_s (%)	P_{tis} (%)	PO_4–P (μg-at/liter)	Avail.N	P_n (%)	P_{tisn} (%)	Calculated net C fixation (g/m²/day)	Per cent of total net photosynthesis	Net photosynthesis (g/m²/day)*
Sept.	7560	17	72	31.9	80	57	0.34	0.82	46	26	.131	84	.156
Oct.	6200	15	48	32.5	78	37	0.55	1.7	54	20	–	–	–
Nov.	2860	14	27	33.1	77	21	0.62	2.0	56	12	–	–	–
Dec.	2300	12	16	33.1	77	12	0.62	3.6	64	8	.596	101	.557
Jan.	2720	8	7	33.2	76	5.3	0.75	3.5	65	3	–	–	–
Feb.	2410	5	3	33.2	76	2.3	0.74	3.35	62	1.5	.072	13	.550
Mar.	6180	6	7	33.0	76	5.3	0.60	2.22	58	3	.000	0	.109
Apr.	8330	6	8	33.1	77	6.2	0.60	1.7	57	4	–	–	–
May	8520	8	16	33.1	77	12	0.48	1.25	50	6	.000	0	.106
June	7880	13	38	32.8	78	30	0.45	1.7	52	15	–	–	–
July	7200	17	72	32.5	78	56	0.33	1.8	51	29	.101	2	.500
Aug.	7400	16	60	32.6	78	47	0.33	1.5	50	24	–	–	–
Sept.	7610	16	63	32.7	78	49	0.32	1.01	50	25	–	–	–

* Calculated from Ryther and Yentsch (1958).

† Underlined months are those for which hydrographic data are available. Others are extrapolated.

TABLE V. The Fractions (P) of Maximum Photosynthesis Computed Successively for Temperature and Light (t, i), Salinity (s), and Nutrients (n). The Cumultative Effect (Potential Photosynthesis) is Given by the Product of These (P_{tisn}).

Data for Stations with Water Depths of from 100 to 500 m.

Date†	Light (lux)	Temp (°C)	P_{ti} (%)	Salinity (‰)	P_s (%)	P_{tis} (%)	PO_4–P (μg-at/liter)	Avail.N (μg-at/liter)	P_n (%)	P_{tisn} (%)	Calculated net C fixation (g/m²/day)	Per cent of total net photosynthesis	Net photosynthesis (g/m²/day)*
Sept.	8060	19	92	34.6	74	68	0.12	0.94	45	31	.001	0.5	0.19
Oct.	6590	18	77	34.4	74	57	0.20	1.50	48	26	–	–	–
Nov.	2090	15	25	33.4	77	19	0.40	2.50	54	10	–	–	–
Dec.	1670	15	15	34.0	74	11	0.50	4.15	64	7	.012	2	0.52
Jan.	1980	12	11	34.3	74	8	0.62	5.2	68	5	–	–	–
Feb.	1890	9	7	34.2	74	5	0.62	6.1	74	5	.025	15	0.16
Mar.	2600	8	9	33.8	76	7	0.52	3.42	60	4	.000	0	1.60
Apr.	2180	9	9	34.0	74	7	0.62	2.8	45	3	–	–	–
May	2240	10	10	34.1	75	8	0.41	1.05	50	4	.000	0	0.71
June	4810	13	32	33.8	76	24	0.30	1.00	50	4	–	–	–
July	7450	16	61	33.5	77	47	0.25	0.94	46	21	.000	0	0.37
Aug.	7330	17	72	33.9	76	55	0.35	2.00	52	28	–	–	–
Sept.	7900	17	73	34.3	74	54	0.52	3.1	60	32	–	–	–

* Calculated from Ryther and Yentsch (1958).

† Underlined months are those for which hydrographic data are available. Others are extrapolated.

TABLE VI. The Fractions (P) of Maximum Photosynthesis Computed Successively for Temperature and Light (t, i), Salinity (s) and Nutrients (n). The Cumulative Effect (Potential Photosynthesis) is Given by the Product of These (P_{tisn}).

Data for Stations with Water Depth of from 500 to 2000 m.

Date†	Light (lux)	Temp (°C)	P_{ti} (%)	Salinity (‰)	P_s (%)	P_{tis} (%)	PO_4–P (μg-at/liter)	Avail.N (μg-at/liter)	P_n (%)	P_{tisn} (%)	Calculated net C fixation (g/m²/day)	Per cent of total net photosynthesis	Net photosynthesis (g/m²/day)*
Sept.	9230	23	88	35.6	73	64	0.13	0.55	45	29	0	0	0.21
Oct.	7550	21	97	35.5	72	70	0.20	1.00	47	33	–	–	–
Nov.	1090	18	17	35.0	75	13	0.30	2.00	52	7	–	–	–
Dec.	870	16	3	35.2	72	2	0.36	3.09	57	1.2	.000	0	0.18
Jan.	1040	14	15	35.4	72	11	0.53	5.6	72	8	–	–	–
Feb.	830	13	1	35.5	72	0.7	0.62	6.5	71	0.5	.000	0	0.10
Mar.	590	15	0	36.1	71	0	0.52	5.3	67	0	.000	0	0.56
Apr.	590	14	0	35.8	73	0	0.50	3.70	65	0	–	–	–
May	600	13	0	35.3	72	0	0.35	1.73	50	0	0	0	1.03
June	3950	17	45	35.2	72	32	0.25	1.00	47	15	–	–	–
July	7310	20	100	35.0	75	75	0.12	0.84	45	34	0	0	0.19
Aug.	5750	20	100	35.5	72	72	0.13	0.90	46	33	–	–	–
Sept.	4750	20	100	36.0	71	71	0.19	0.92	46	33	–	–	–

* Calculated from Ryther and Yentsch (1958).

† Underlined months are those for which hydrographic data are available. Others are extrapolated.

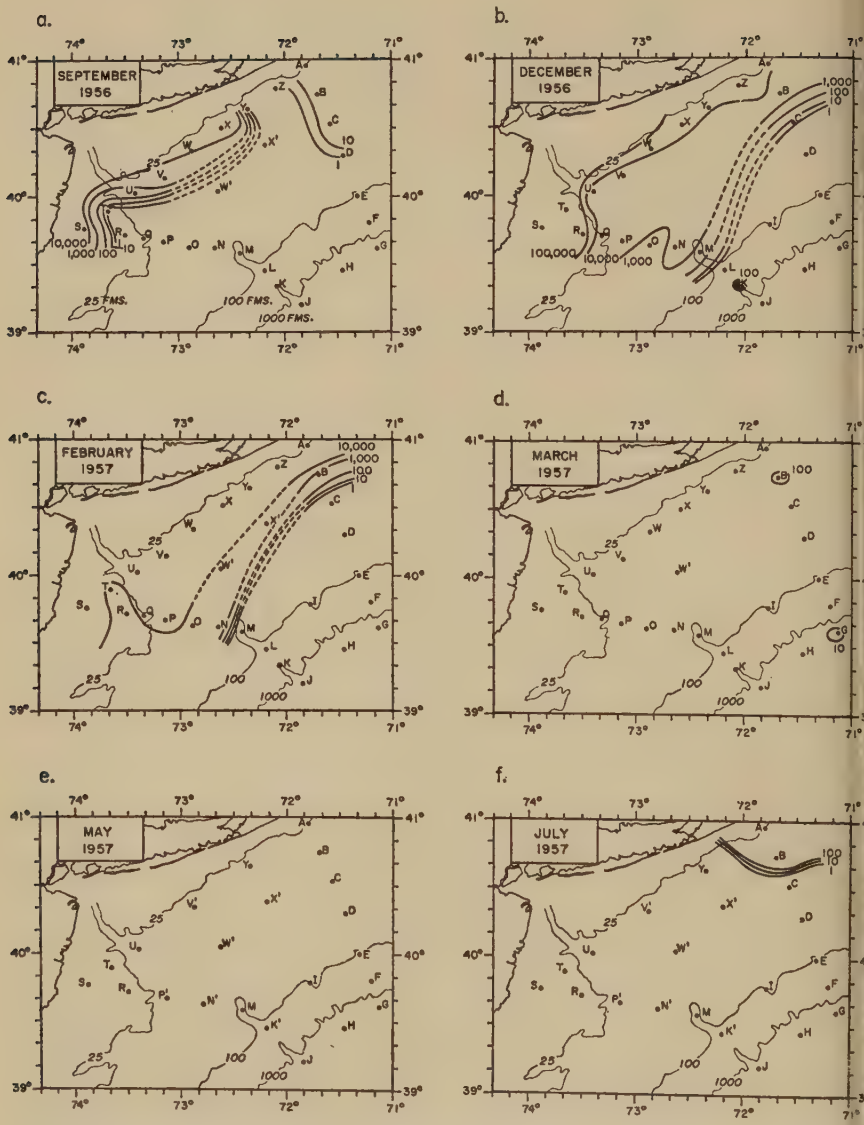


Figure 5 a–f. Distribution of *Skeletonema* (cells per liter) at 10 m depth on the continental sh
from September 1956 to July 1957.

s period. Likewise, the almost complete absence of cells from March onward responds with the calculated lack of photosynthesis by *Skeletonema* during s period. The appearance of a small bloom in July is in accordance with prediction of an increase in *Skeletonema* photosynthesis in early summer able IV).

It would be ideal to be able to compare calculated potential photosynthesis h actually measured photosynthesis of the species, but only the total phytonkton photosynthesis is available (last column, Tables IV, V, and VI).

For the shallow waters, at least, light and temperature appear to be the ntrolling influences on the seasonal appearance of *Skeletonema* whereas the e of the standing crop is controlled by an interaction of all the factors.

The fact that the population continues to increase from September through cember may be explained by the supposition that the standing crop reflects ime lag between the environmental conditions and their expressions. Zoonkton grazing may be implicated also. Riley (1956) calculated that 65% the phytoplankton produced in Long Island Sound was consumed by pelagic ganisms. Our evidence indicates that *Skeletonema* is readily eaten by small pepods in "preference" to some other genera. Zooplankton volumes avered 46% lower in the November-December cruise than in the September ise. Volumes in February and March increased and were greatest in March url, unpublished). Cladocera and copepods predominated in the samples. razing appears to be a plausible explanation of reduced cell numbers in ptember.

The intermediate and deep stations never supported large standing crops *Skeletonema* despite good conditions for growth. Because zooplankton lumes were low at these stations, some factor not considered thus far must limiting. Since the diatom is so obviously a neritic species, despite good owth conditions on the deep shelf, the factor (s) may be associated with oximity to either the benthos or land. *Skeletonema* requires both vitamin B_{12} Droop 1955) and divalent sulfur (Lewin, personal communication), among ner nutrients. The seaward advection, dilution by mixing, and biological struction of such substances would make them unavailable to it on the deep elf and would help to account for its observed spatial distribution.

Calculated zero potential photosynthesis at deep stations is indicative of ep mixing below the euphotic zone in winter (50% of the population may below the compensation depth). However, when the thermocline is present, e potential photosynthetic rates are frequently more than double those close shore. Nevertheless, *Skeletonema* is absent from offshore waters. One reason that virtually no photosynthesis is possible during seven months of the year, d it has been shown that cells of *S. costatum* can survive only two months darkness. Matsue (1954) found that *Skeletonema* could be kept in the dark to 52 days without high mortality but that no cells survived beyond 60 days. ur experience agrees with this result. Moreover, if some substance derived

from land drainage is essential for growth, it is even less likely to be found a the deep stations.

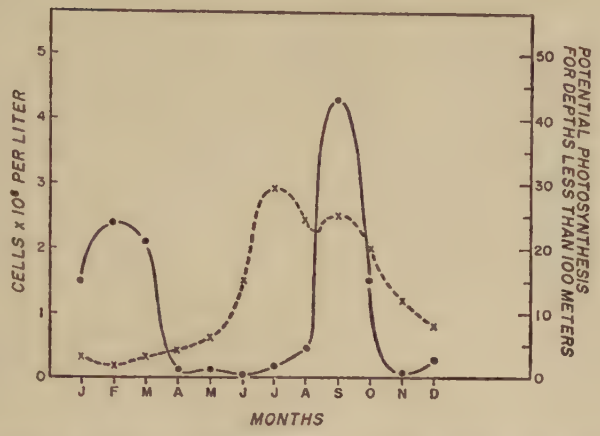
The circulation out of the lighted zone in winter is a condition to whic almost all oceanic algae are subjected. A necessary consequence is that oceani species must be able to tolerate periods of low illumination.

The photosynthesis of observed natural populations of *Skeletonema* can b estimated from our data. The maximum carbon fixation per cell is known fro laboratory experiments, and the potential fraction of this value for each mont has been calculated. These multiplied by the average cell concentration giv the estimated carbon fixation by *Skeletonema* in nature. The highest photo synthetic rate observed in the laboratory was 1.76×10^{-3} mg C/10^4 cells/hou calculated from C^{14} uptake. (*Chlorella*, which has one of the highest photo synthetic rates known, has a maximum reported rate of 16×10^{-3} mg C/hr/μ cell volume [Hill and Whittingham 1957] whereas *Skeletonema* fixed 2.8×10^{-3} mg C/hr/μl cell volume in our experiments.) The net carbon fixation a each station may be derived from the formula:

(cells/m^3) $\times$ (1.76×10^{-7} mg C) $\times$ (hrs daylight) $\times$ (m depth) $\times$ (% max. photo synthesis) = gC/m^2/day.

The depth used in this calculation is that of the mixed layer as previously use In tables V–VII these computed values are compared with the observed tot phytoplankton net photosynthesis computed from the data of Ryther an Yentsch (1958). A maximum of 0.596 gC fixed/m^2/day by *S. costatum* i calculated for December at the shallow stations. These rates correspond t 100% of the observed fixation for this area and time. *Skeletonema* also coul have accounted for 84% of the carbon fixation in September 1956. Durin the period of greatest carbon fixation, in March and May, it was not present The comparative absence of *S. costatum* cells at the intermediate and dee stations throughout the year accounts for their lack of contribution to the tot phytoplankton production.

Thus far, data for the seasonal occurrence of *Skeletonema* for one year hav been examined. From similar data from inshore waters in other years it ma be determined if the distribution of 1956–1957 was typical. Cell counts o *Skeletonema* from Vineyard Sound 1950–1951, Woods Hole 1956–195 (Hulburt, unpublished), Narragansett Bay 1954–1955 (Smayda 1957), Bloc Island Sound 1949 (Riley 1952), Vineyard Sound 1935 (Lillick 1937), an Long Island Sound 1952–1954 (Conover 1956), were averaged for eac month of the year irrespective of year or geography. Although the actu counts range from 0 to 20×10^6 cells per liter at any one particular place an time, the averages plotted against time yield a smooth bimodal curve (Fig. 6 The outstanding difference between the postulated shelf pattern and th inshore observations is the bimodal nature of the latter. The late autumn an winter peak occurs on the shelf but lags behind the high summer potentia


CELLS x 10⁴ PER LITER
POTENTIAL PHOTOSYNTHESIS FOR DEPTHS LESS THAN 100 METERS
MONTHS
J F M A M J J A S O N D
0 1 2 3 4 5
0 10 20 30 40 50

igure 6. Averaged *Skeleotnema* concentrations in the inshore waters of the northeastern states, and calculated potential photosynthesis. Solid line, cell concentration; dashed line, potential photosynthesis.

pring bloom of this species does not ordinarily occur in the self waters. For mple, Bigelow (1926) says, this genus is ". . . closely confined to the im- diate vicinity of the land in the Gulf of Maine and to the shallow water he banks, where it flowers irregularly during summer and early autumn. . . north European waters it has its maximum in spring but has been found vering in autumn as well at many localities." The inshore spring flowering e and possibly the spring flowering in Europe must be a response to a factor studied.

Conover (1956) and others have noted that *Thalassiosira nordenskioldii* Cl. urs under nearly the same conditions as does *Skeletonema* and seems to be closest competitor. The optima of light and temperature for the growth *Skeletonema* are higher than those for *Thalassiosira*. Ryther (1956 a) derived average relationship between light intensity and photosynthesis from studies several species of diatoms, and a comparable curve has been derived for *Skele- ema* (Fig. 7). In the summertime *Skeletonema* tends to be favored by shade npared to the "average diatom" and would be inhibited at light intensities eeding 25% of the surface value. If the mixed depth was as deep as the npensation depth or deeper, then *Skeletonema* would be able to equal the y production of the "average diatom". In December, however, *Skeletonema* aves like an "average diatom" at 12°C and can be significantly more pro- tive than the average at 16°C. From a competitive viewpoint *Skeletonema* uld fare best in early winter, and it certainly seems to do so

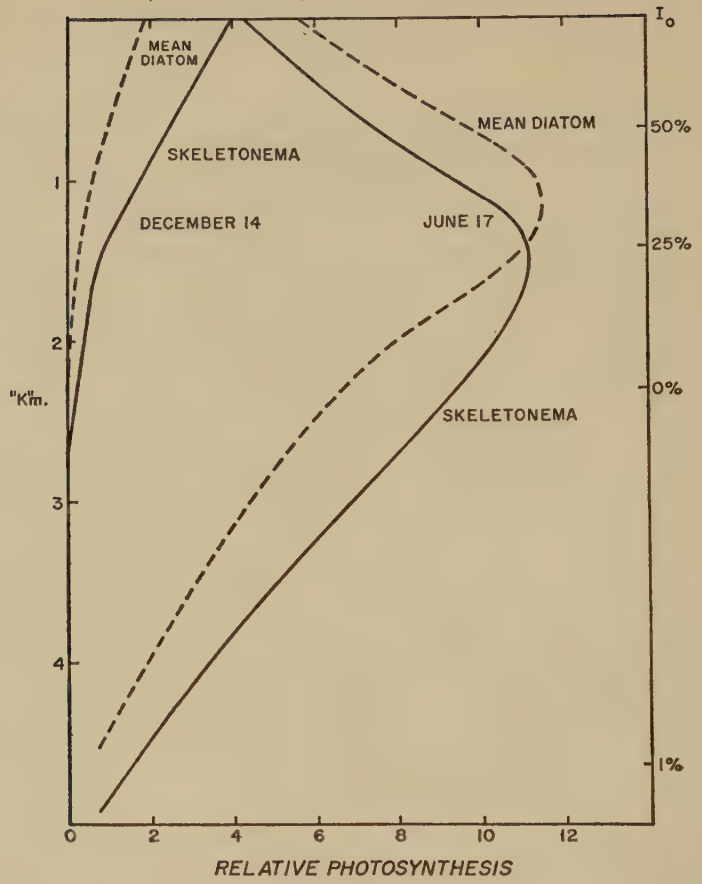


Figure 7. Integrated relative daily photosynthesis of *Skeletonema* as compared to that of the me values for diatoms in general.

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'mino Acids in Samples of Surface Sea Water[1]

Mitsunobu Tatsumoto[2], W. T. Williams, J. M. Prescott, and Donald W. Hood

Department of Oceanography and Meteorology and Department of Biochemistry and Nutrition, Agricultural and Mechanical College of Texas

ABSTRACT

Both paper and ion exchange chromatographic techniques have been used to identify l make a partial quantitative estimate of amino acids in surface water samples collected four subtropical regions. The most abundant of the 18 amino acids identified were artic acid, threonine, serine, glutamic acid, alanine, valine, isoleucine, and leucine. general, basic amino acids, possibly except for lysine, seem to be in low concentra-n. The amino acid composition of hydrolysates of proteinaceous material in sea water ies in the samples. These differences may be important in the ecology of marine anisms.

Interest in the dissolved organic compounds in sea water has increased ently because of their importance in the nutrition of phytoplankton, the logy of marine organisms, the geochemistry of petroleum and marine sedi-nts, and in other environmental phenomena such as surface adsorption, the mation of slicks, and trace element chelation. Saunders (1957) and Vallen-ne (1957) have written review articles on the soluble organic compounds ich have been identified in natural environments, including sea water.

Biochemical substances in sea water have been separated from sea salt by vent extraction, dialysis, or adsorption: the isolation of vitamin B_{12} by wey (1956), the identification of organic acids of low molecular weight Koyama and Thompson (1959), and the quantitative estimation of fatty ds in vertical profiles of the ocean by Slowey *et al.* (1959) and Williams 961). Belser (1959) has used biochemically deficient mutant strains of cteria for direct evaluation of the organic micronutrient content of sea water.

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[2] Present Address: California Institute of Technology, Pasadena, California.

The importance of proteins, peptides, and amino acids in sea water ha long been recognized. Neuberg *et al.* (1957) have indicated the importanc of proteinaceous material in the formation of carbamino carboxylic acids, fact which may be significant in the marine geochemistry of calcium carbonat Smith *et al.* (1960) have shown that the carbamino carboxylic acids are preferred source of carbon dioxide for many marine phytoplankton. Large because of the difficulties in separating dissolved proteinaceous material fro sea salt, identification of these compounds has been extremely limited (Belse 1959). Several amino acids have been identified in marine sediments by Erdma *et al.* (1956) and in older sediments by Abelson (1955). Fogg (1952) an Watanabe (1951) identified the amino acids in the filtrate of algal culture Evidence for proteins in sea water has been reported by Anderson *et al.* (1956

Jeffrey and Hood (1958) have indicated that coprecipitation of organ matter with ferric hydroxide is an effective means of isolating a large portio of the organic materials from sea water. The purpose of the investigation he reported was to identity amino acids derived from acid hydrolysates of s water concentrates which were isolated by this technique.

TABLE I. Sampling Locations; All Samples Taken at the Surface.

Region	Location	Depth (m)	Volume o Sample (L
Gulf of Mexico.....	25°20′N, 90°24′W	1950	75
Yucatán Strait	25°20′N, 86°07′W	1200	75
Reef near British Honduras ...	17°05′N, 88°09′W	9.7	37.5
Caribbean Sea	21°33′N, 85°57′W	1050	75

Preparation of Samples. Four samples of sea water collected from the surfa (see Table I) were filtered through a 0.45 μ Millipore filter within eig hours of collection. To each liter of water, 0.015 g of mercuric chloride w added and to each 18 liters, 20 ml of 2 M ferric chloride. The soluble organ fraction was coprecipitated with ferric hydroxide by adding 40 ml of 2 sodium hydroxide. Upon our return to the laboratory, the iron precipita was filtered through a 5 cm glass wool filter mat and dissolved in excess 6 hydrochloric acid. This solution was hydrolyzed for 24 hours by refluxi at atmospheric pressure, then concentrated *in vacuo* at less than 70°C to redu the volume and remove part of the hydrochloric acid. The concentrat solution, after being adjusted to pH 1 with NH_4OH, was passed throu 2.5 L (7.5×55 cm column) of Dowex 50-X8 cation exchange resin in t hydrogen form. The loaded column was washed with 3 L of 0.1 N HCl a eluted with 8 L of 2 N NH_4OH. The eluate was concentrated to 500 m *in vacuo* at less than 60°C and loaded on 100 ml of IRA-400 anion exchan resin in the chloride form (2×30 cm column). After the column had be washed with 200 ml of distilled water, the amino acids were eluted with 500 m

1 N HCl. The material was then placed in the refrigerator for future use. n aliquot of 100 ml of the eluate was frozen and dried, then dissolved in nl of 10% isopropyl alcohol, and used for paper chromatography. Another quot, reduced in volume, was used for ion exchange chromatographic paration of the amino acids.

paration by Paper Chromatography

A. One-dimensional separation. Aspartic acid, glutamic acid, cystine, and reonine were identified by development on Whatman No. 3 filter paper. he solvent used was phenol: water in an 80:20 mixture, with a small quantity 8 hydroxy-quinoline having been added to the phenol prior to addition of ter; beakers containing 10 ml of 1% NaCN and 25 ml of 0.3% ammo- um hydroxide were placed in the chromatogram chamber. A 0.2% nin- drin solution in acetone was used as the detecting agent.

Lysine, histidine, arginine, alanine, isoleucine, and leucine were identified th normal butanol: acetic acid: water in a 240:60:250 mixture. The upper er was separated and used as a moving phase; the lower layer was placed in e chromatogram chamber.

Proline was identified with butanol: acetic acid: water in a 450:50:125 xture. The color reagent used was 0.2% isatine in acetone. The color was veloped after addition of the reagent to air-dried chromatographic strips by ating in an oven at 70°C for 10 minutes.

B. Two-dimensional separation. Here the solvent system was methanol: ter: pyridine in the ratio 80:20:4, followed by *t*-butanol: methyl ethyl- tone: water: diethylamine in the ratio 40:40:20:4. Boric acid buffer was ded to maintain a pH of 9.2; and a 0.2% ninhydrin solution in acetone was ed to identify the amino acid spots.

Separation by Ion Exchange Chromatography. Amberlite CG 120 cationic change resin was graded to the correct particle sizes by the hydraulic flow ethod of Hamilton (1958) and was used to fill two columns, one 0.9×150 cm d the other 0.9×50 cm. The procedure used for amino acid analysis was ntical to that of Moore *et al.* (1958), which is briefly described as follows: 1–2 ml sample containing an amino acid mixture or protein hydrolysate s pipetted on the 150 cm column, and elution was begun with 0.2 N citrate ffer at pH 3.25 and a temperature of 30°C. Upon emergence of alanine m the column (approximately 300 ml effluent volume), the eluting buffer was raised to 4.25 and the temperature was increased to 50°C. This ocedure served to separate the neutral and acidic amino acids.

In order to determine the basic amino acids, an identical sample was put the 0.9×50 cm column and elution was begun with 0.38 N sodium citrate ffer at pH 4.26 and 30°C. After 400 ml of effluent had been collected,

the temperature was raised to 50°C, with a simultaneous change to anothe 0.38 N citrate buffer whose pH was 6.25. The type of separation provide by this procedure in our hands is shown in Fig. 1, which represents a recover experiment with a known mixture of amino acids.

Recovery of Proteinaceous Material from Sea Water. The isolation of fre amino acids in sea water by coprecipitation with ferric hydroxide was invest gated with phenylalanine-3-C^{14}, and 53% of this amino acid was recovere Jeffrey and Hood (1958) have found that nearly 100% of the total organi material in aged algal cultures is removed by the process of ferric hydroxid coprecipitation. However, it is believed that the free amino acids in sea wat are present in very small quantities compared to the combined amino aci such as the proteins and peptides.

The demineralization of sea water by means of Dowex resin and IRA-40 using C^{14}-labeled methionine indicates that 96% of this amino acid is re covered from these resins by the technique used. Very small amounts of th basic amino acids were found in these hydrolysates; it is possible, therefor that some of these were lost by incomplete adsorption on the IRA-400 resi

TABLE II. Summary of the Results of Paper Chromatographic Studies o Amino Acid Composition of Acid Hydrolysates of Sea Water.

Region	Isoleucine	Leucine	Glutamic Acid	Alanine	Aspartic Acid	Valine	Cystine	Arginine	Histidine	Lysine	Serine	Proline
Gulf of Mexico....	+++	+++	+++	++	++	+	+	±	±	±	±	±
Yucatán Strait.....	+	+	+	−	−	−	+	−	−	−	−	−
Reef near British Honduras	+++	+++	++	++	±	+	+	±	−	−	−	−
Caribbean Sea	+++	+++	++	++	+	+	+	−	±	−	−	−

± Indicates that a spot occurred at the proper R_f value for the respective amino ac but that positive identification was not made.

Results. The results presented in Table II were obtained with a comb nation of solvents and one- and two-dimensional techniques. The data sho positive identification of isoleucine, glutamic acid, and cystine, in all th samples studied. Since the sample from the Yucatán Strait shows a much low concentration of amino acids than do the others, it is likely that the quantiti present in it were too small to identify.

Ion exchange analysis of hydrolysates provides a resolution of the amin acid fraction, and if the concentration level is adequate, it also permits a quant tative estimate of the amino acids present. Our analysis of water samples fro

TABLE III. Ion Exchange Analysis of Amino Acid Composition of Hydrolysates of Surface Ocean Water.

Amino Acids	Gulf of Mexico* (mg/M³)	Reef near British* Honduras (mg/M³)
bartic Acid	+	++
reonine	++	+
ine	+	++
tamic Acid (and/or Citrulline)	+++	++++
rcine**	+	++
nine**	+	++
ine†	+	++
thionine	+	–
eucine	+	++
cine	+	+
rosine	+	+
ine	+	++
tidine	+	+
ptophan	+	+
ginine	+	–
ithine	+	+
teic acid or Phosphoethanolamine	+	+
cosamine	+	–

* Trace-3 mg/M³: +; 3–8: ++; 8–13: +++; 13– : ++++; –: not detected.
** Not well resolved.
† May be more than one component.

Gulf of Mexico and the reef near British Honduras (Table III) shows amino acid composition of the hydrolysates to be quite variable. It may inferred that the peptides and proteins, from which most of the amino ds are thought to be derived, vary considerably in these two samples. Data re also obtained by ion exchange techniques from the Yucatán and Caribbean mples, but the concentration of amino acids was too low for reliable results. owever, enough information was gained to indicate that these samples differ amino acid content from the other pair of samples.

Summary. It seems reasonable to infer, at least for surface water, that there ariation in the organic nitrogen components. In general, basic amino acids, th the possible exception of lysine, seem to be in low concentration. Of 18 ino acids identified in four samples, the most abundant were aspartic acid, eonine, serine, glutamic acid, alanine, valine, isoleucine, and leucine. fferences in amino acid content may have importance in the ecology of anisms depending on this source of nutrients or stimulants for growth. uch more work is needed to determine the differences in amino acid com- ition of both surface waters and sub-surface waters collected in vertical files.

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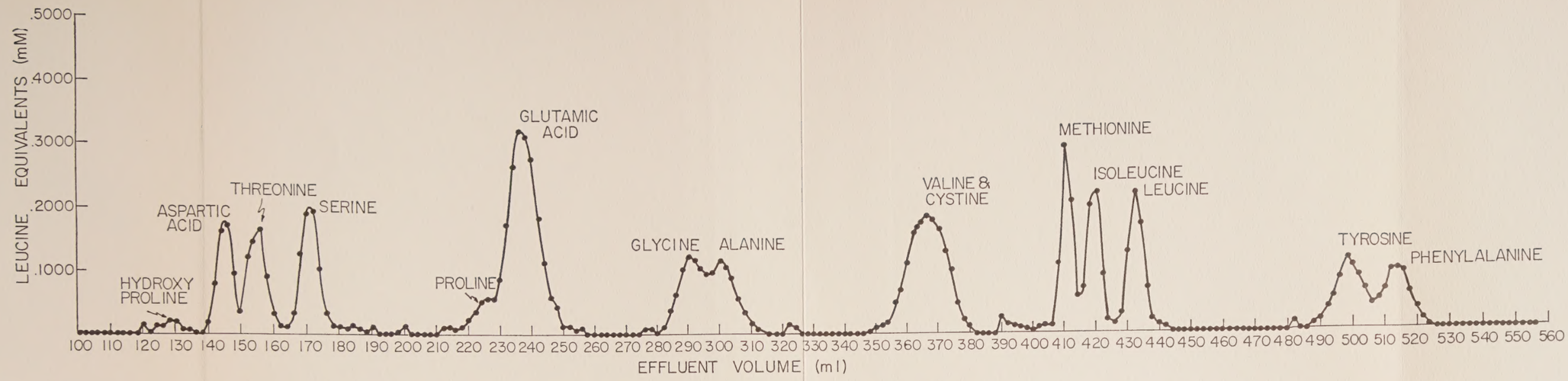

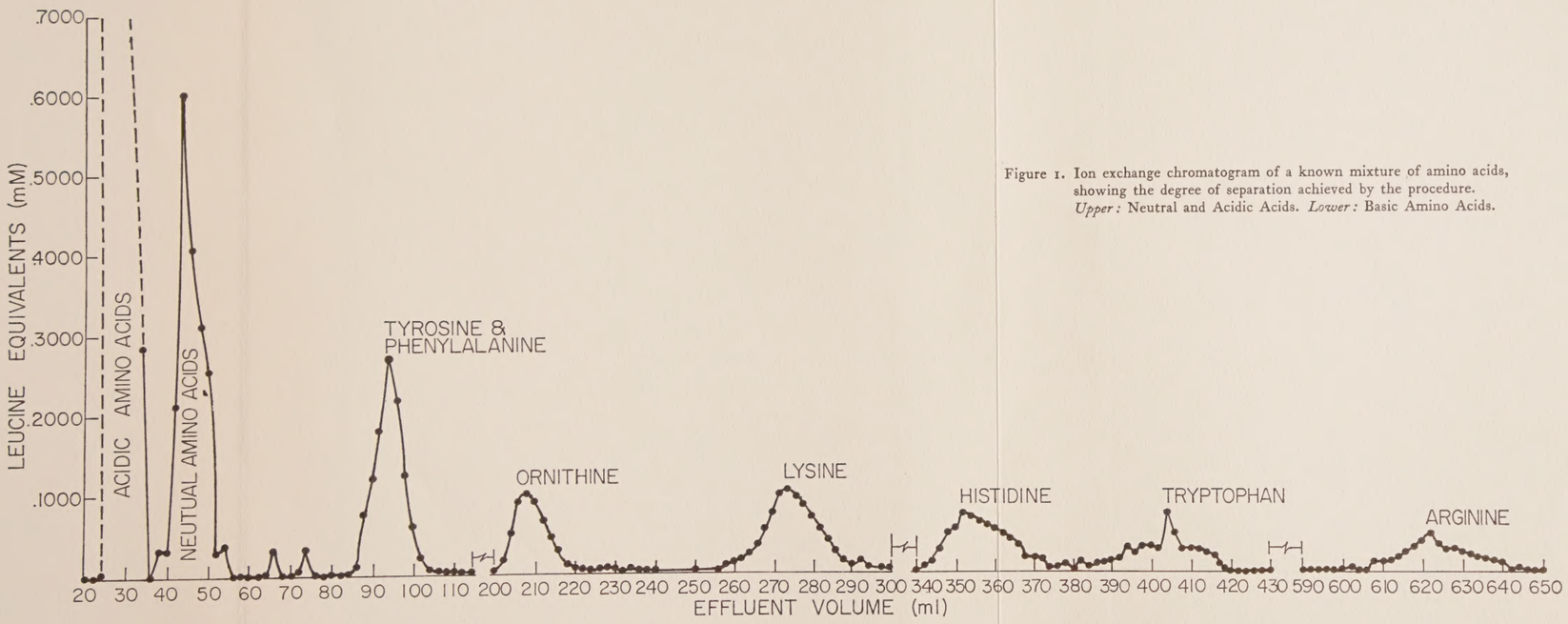

Figure 1. Ion exchange chromatogram of a known mixture of amino acids, showing the degree of separation achieved by the procedure. *Upper:* Neutral and Acidic Acids. *Lower:* Basic Amino Acids.